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Bulky *ortho*-disubstituted phenolates of magnesium, calcium and zinc: structural features and comparison of catalytic properties in polymerization of ε-caprolactone and *rac*-lactide

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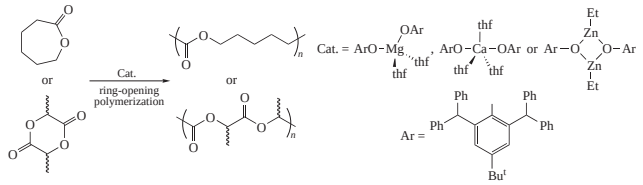
Complexes of Mg, Ca and Zn based on sterically hindered 4-*tert*-butyl-2,6-bis(diphenylmethyl)phenol were synthesized and tested as catalysts of ring-opening polymerization of ε-caprolactone and *rac*-lactide.

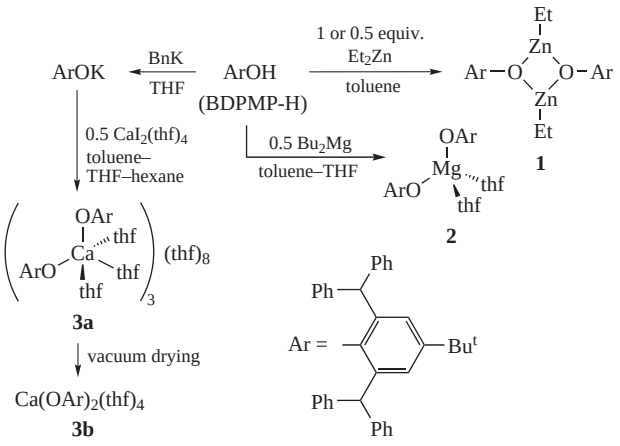


Phenolates of non-toxic metals are prospective catalysts of cyclic ester ring-opening polymerization (ROP).[1–11] *ortho*-Disubstituted bulky phenols, including 2,6-di-*tert*-butyl-4-methylphenol (BHT-H), were successfully used in synthesis of highly active catalysts.[3–10] Phenolates of BHT-H type demonstrate extremely high productivity, which complicates the conducting of comparative experiments.[3,9] To properly perform such experiments, it is better to use less active catalysts, for example, derivatives containing more bulky ligands than BHT. We chose 4-*tert*-butyl-2,6-bis-(diphenylmethyl)phenolate (BDPMP)[12] as one of such ligands, for which only *d*-metal derivatives were synthesized and described.[12–16] The purpose of this study was to analyze and compare the molecular structures and catalytic properties of BDPMP complexes of Mg, Ca and Zn.

Complex $[Zn(Et)(\mu\text{-BDPMP})]_2$ **1** was obtained by the reaction of Et_2Zn with BDPMP-H[12] in a ratio of 1 : 1 in toluene. The same product **1** was formed in the case of the reagent ratio of 1 : 2. A reaction of Bu_2Mg with BDPMP-H in a 1 : 2 ratio in the presence of THF afforded monomeric complex $Mg(BDPMP)_2(thf)_2$ **2**. Crystalline $[Ca(BDPMP)_2(thf)_3]_3(thf)_8$ **3a** was obtained from $CaI_2(thf)_4$[17] and two equivalents of BDPMP-K. Drying **3a** under dynamic vacuum led to partial loss of non-coordinating THF molecules, which resulted in the formation of $[Ca(BDPMP)_2(thf)_3]$(thf) **3b**. Syntheses of **1**–**3** are presented in Scheme 1.

Complexes **1**, **2** and **3a** were studied by the single crystal diffraction.† The structure of dimeric molecule $[Zn(Et)(\mu\text{-BDPMP})]_2$ [Figure 1(*a*)] is analogous to that of other (ArO)M(Alkyl) complexes.[9,18–22] The Zn atom is in a trigonal coordinative environment. In the monomeric complex $Mg(BDPMP)_2(thf)_2$ [Figure 1(*b*)], the Mg atom is in a distorted tetrahedral environment. Mg–O–C_{Ar} angle values are close to the straight angle.

The crystal unit cell of **3a** contains two crystallographically independent molecules of $Ca(BDPMP)_2(thf)_3$ (Figure 2) with coordination number 5 for Ca. One molecule [Figure 2(*a*)] is located on a 2-fold proper rotation axis passing through Ca(1)



Scheme 1

† *Crystallographic data for* **1**: $C_{76}H_{76}O_2Zn_2$, M = 1152.11, triclinic, space group $P\bar{1}$, a = 9.9899(6), b = 12.4807(7) and c = 12.9874(8) Å, α = = 78.7194(8)°, β = 76.8591(8)°, γ = 77.0231(8)°, V = 1518.7(2) Å^3, Z = 1, d_{calc} = 1.260 g cm^{-3}, $F(000)$ = 608, μ(MoKα) = 0.837 mm^{-1}, T = 150(2) K, 2.42° < θ < 29.00°. Total of 17000 reflections were measured, from which 8042 reflections were independent (R_{int} = 0.0196), 513 parameters were used in calculations. Final R indices are: R_1 = 0.0314, wR_2 = 0.801 [for 7087 reflections with $I > 2\sigma(I)$]; R_1 = 0.0369, wR_2 = 0.0827 (all data). GOF = 1.062, largest diff. electron density, peak/hole: 0.465/–0.256 e Å^{-3}.

Crystallographic data for **2**: $C_{80}H_{82}O_4Mg$, M = 1131.77, triclinic, space group $P\bar{1}$, a = 12.724(2), b = 15.002(2) and c = 17.216(2) Å, α = 81.878(2)°, β = 87.480(2)°, γ = 86.280(2)°, V = 3244.6(8) Å^3, Z = 2, d_{calc} = 1.158 g cm^{-3}, $F(000)$ = 1212, μ(MoKα) = 0.078 mm^{-1}, T = 150(2) K, 2.39° < θ < 26.00°. Total of 29029 reflections were measured, from which 12734 reflections were independent (R_{int} = 0.0360), 772 parameters were used in calculations. Final R indices are: R_1 = 0.0473, wR_2 = 0.1045 [for 8631 reflections with $I > 2\sigma(I)$]; R_1 = 0.0814, wR_2 = 0.1181 (all data). GOF = 1.017, largest diff. electron density, peak/hole: 0.315/–0.277 e Å^{-3}.

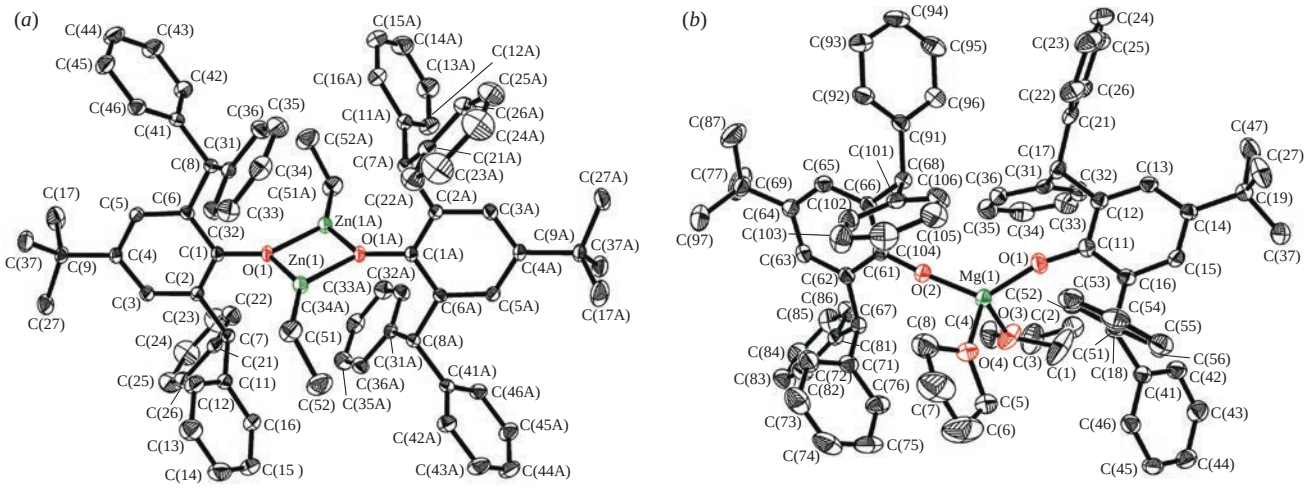


Figure 1 Crystal structure of (*a*) [Zn(Et)(μ-BDPMP)]$_2$ **1** and (*b*) [Mg(BDPMP)$_2$(C$_6$H$_2$)$_2$(thf)$_2$] **2**. Displacement ellipsoids are shown at 50% probability level. H-atoms are omitted. For **1**: selected distances (Å): Zn(1)–O(1) 1.9527(9), Zn(1)–O(1A) 1.9863(9), Zn(1)–Zn(1A) 3.0239(3), Zn(1)–C(51) 1.941(2), O(1)–C(1) 1.374(1); selected bond angles (°): O(1)–Zn(1)–C(51) 144.87(6), O(1A)–Zn(1)–C(51) 135.15(6), O(1)–Zn(1)–O(1A) 79.71(4), Zn(1)–O(1)–Zn(1A) 100.29(4), C(1)–O(1)–Zn(1) 127.00(8), C(1)–O(1)–Zn(1A) 132.69(8). Symmetry transformation: (A) [–*x* + 1,–*y* + 1, –*z* + 1]. For **2**: selected bond lengths (Å): Mg(1)–O(1) 1.852(1), Mg(1)–O(2) 1.838(1), Mg(1)–O(3) 2.027(2), Mg(1)–O(4) 2.014(2), O(1)–C(11) 1.328(2), O(2)–C(61) 1.322(2); selected bond angles (°): O(1)–Mg(1)–O(2) 127.32(6), O(1)–Mg(1)–O(3) 102.96(7), O(1)–Mg(1)–O(4) 108.29(6), O(2)–Mg(1)–O(3) 110.12(6), O(2)–Mg(1)–O(4) 103.09(6), O(3)–Mg(1)–O(4) 102.64(7), C(11)–O(1)–Mg(1) 160.79(12), C(61)–O(2)–Mg(1) 174.86(12).

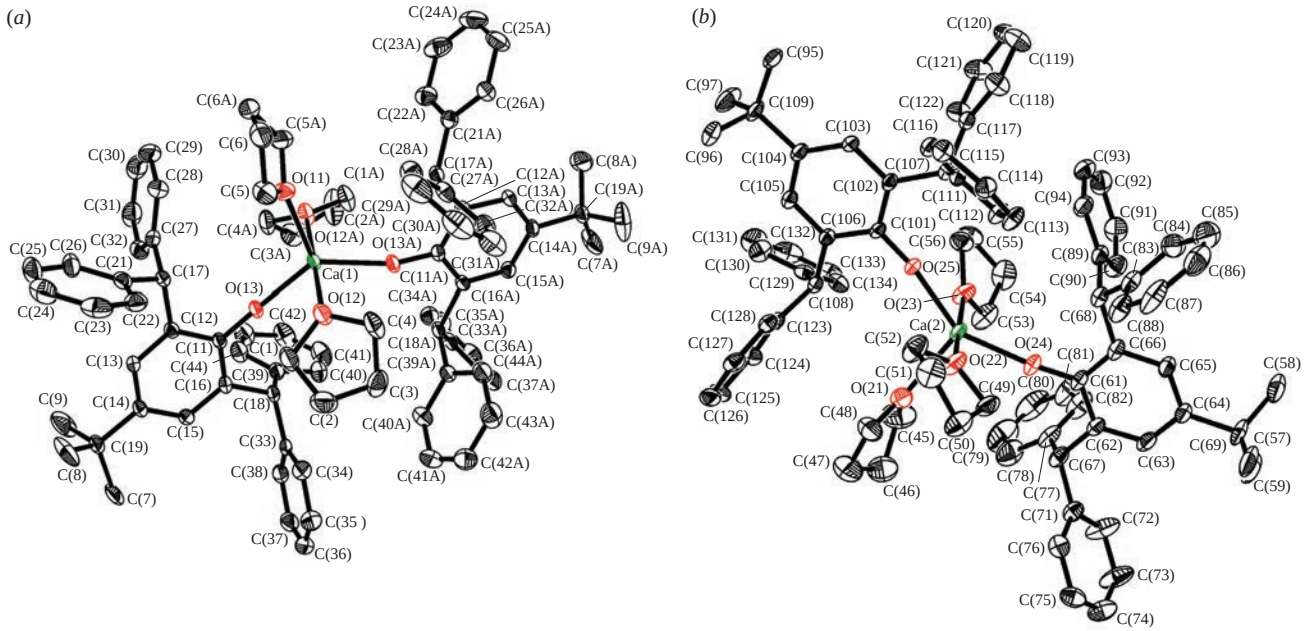


Figure 2 Two independent [Ca(BDPMP)$_2$(thf)$_3$] molecules (*a*) and (*b*) in **3a**. Displacement ellipsoids are shown at 30% probability level. H-atoms and minor components of disordered groups are omitted for clarity. Selected bond lengths (Å): Ca(1)–O(11) 2.389(4), Ca(1)–O(12) 2.380(3), Ca(1)–O(13) 2.148(3), O(13)–C(11) 1.321(5), Ca(2)–O(21) 2.371(4), Ca(2)–O(22) 2.351(4), Ca(2)–O(23) 2.351(4), Ca(2)–O(24) 2.150(3), Ca(2)–O(25) 2.152(3), O(24)–C(61) 1.315(5), O(25)–C(101) 1.318(5). Selected bond angles (°): C(11)–O(13)–Ca(1) 162.9(3), O(11)–Ca(1)–O(12) 90.30(9), O(11)–Ca(1)–O(13) 113.73(8), O(12)–Ca(1)–O(12A) 179.4(2), O(12)–Ca(1)–O(13) 90.8(1), O(12A)–Ca(1)–O(13) 88.9(1), O(13)–Ca(1)–O(13A) 132.6(2), C(61)–O(24)–Ca(2) 163.9(3), C(101)–O(25)–Ca(2) 169.2(3), O(21)–Ca(2)–O(22) 86.4(2), O(21)–Ca(2)–O(24) 105.3(1), O(21)–Ca(2)–O(25) 107.0(1), O(21)–Ca(2)–O(23) 99.7(2), O(22)–Ca(2)–O(23) 173.1(2), O(22)–Ca(2)–O(24) 88.9(1), O(22)–Ca(2)–O(25) 89.1(1), O(23)–Ca(2)–O(24) 92.4(1), O(23)–Ca(2)–O(25) 86.2(1), O(24)–Ca(2)–O(25) 147.4(1). Symmetry transformation for molecule (*a*): (A) [–*x* + 1, *y*, –*z* + 1/2].

Crystallographic data for **3a**: $C_{284}H_{334}Ca_3O_{23}$, M = 4235.75, monoclinic, space group $C2/c$, a = 53.144(2), b = 12.9177(5) and c = 37.334(1) Å, β = 111.0148(8)°, V = 23925(2) Å^3, Z = 4, d_{calc} = 1.176 g cm^{-3}, $F(000)$ = = 9128, μ(MoKα) = 0.135 mm^{-1}, T = 150(2) K, 2.00° < θ < 25.05°. Total of 88770 reflections were measured, from which 21155 reflections were independent (R_{int} = 0.0746), 1410 parameters and 262 restraints were used in calculations. Final R indices are: R_1 = 0.0939, wR_2 = 0.2508 [for 12666 reflections with $I > 2\sigma(I)$]; R_1 = 0.1508, wR_2 = 0.2910 (all data). GOF = 1.029, largest diff. electron density, peak/hole: 1.307/–0.988 e Å^{-3}.

CCDC 1511142–1511144 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

and O(11) atoms, which makes only a half of the molecule unique. The Ca^{2+} cation of this molecule is in slightly distorted trigonal bipyramidal environment with two THF molecules [containing O(12) and O(12A) atoms] in the axial positions. Due to steric hindrance of the aroxy ligand, the O_{Ar}–Ca(1)–O_{Ar} angle is higher than the O_{Ar}–Ca(1)–$O_{THF(equatorial)}$ angles (see Figure 2). The polyhedron about the Ca(2) atom in the second molecule could be better described as a distorted square pyramid [with O(22), O(23), O(24), and O(25) atoms being a base] rather than a trigonal bipyramid. Note that in **2** and **3a**, O–C_{ipso} distances lie in the range from 1.315(5) to 1.328(2) Å, whereas the length of the same bond in **1** is 1.374(1) Å.

Table 1 Catalytic experimental data for ε-CL and LA polymerization using complexes **1**–**3**.

Catalyst	Monomer	*t*/min	*T*/°C	Conversion *(%)*	$M_{n(th)}$ [a]	M_n, NMR [b]	M_n, SEC [c]	$Đ_M$	P_r [d]
1	ε-CL	10	20	0	0				
1	ε-CL	240	20	15	1800				
1	ε-CL	240	50	27	3200	2600	2700	1.75	
1	LA	200	20	7	1100	400			
1	LA	385	65	78	11300	4100	3800	1.49	0.63
2	ε-CL	10	20	18	2200				
2	ε-CL	240	20	100	11500	11900	12400	1.27	
2	ε-CL	240	50	100	11500	12200	12300	1.54	
2	LA	50	20	20	3000				
2	LA	385	65	96	13900	9100	11300	1.62	0.63
3	ε-CL	10	20	4.5	620				
3	ε-CL	240	20	41	4800	2900	2400	1.39	
3	ε-CL	240	50	100	11500	9200	9400	1.68	
3	LA	10	20	0	0				
3	LA	240	20	17	2600	1200			
3	LA	240	50	97	14100	11200	13400	1.58	0.51

[a] $M_{n(th)} = MW_M \times 100 \times \text{conversion} + MW_I$, where MW_M is molecular weight of monomer, MW_I is molecular weight of initiator. [b] Determined by NMR *via* relative ratio of ^{1}H NMR resonances of polymer terminal group *vs.* polymer methylene (methyne) moieties. [c] Determined by SEC *vs.* polystyrene standards and corrected by a factor of 0.56 for ε-CL and 0.58 for LA.[23] [d] P_r is the probability of racemic placement between monomer units and is determined from the methyne region of the homonuclear decoupled ^{1}H NMR spectrum.[24]

Earlier,[9] we experimentally proved that both (BHT)MgBu and $(BHT)_2Mg$ form ArO–Mg–OR complexes upon activation with alcohol ROH (1 equiv.). We proposed that precatalysts **1**–**3** also form monotypic catalytic particles after activation with benzyl alcohol (BnOH), probably, solvated (BDPMP)M–OBn complexes. We carried out comparative catalytic experiments for 1 M–1 M monomer solutions of ε-caprolactone (ε-CL) and *rac*-lactide (LA) in THF, with a substrate : precatalyst : activator ratio of 100 : 1 : 1. Results are summarized in Table 1.

The most productive complex among **1**–**3** was the Mg complex **2**, for which we observed a full correlation between experimentaly determined number average molecular weight M_n and calculated molecular weight $M_{n(th)}$. Complex **1** demonstrated only moderate catalytic activity. Moreover, at high temperatures the M_n experimentally observed by NMR and SEC was significantly lower (more than twice in the case of LA) as compared to the calculated $M_{n(th)}$. The calcium complex **3** displayed a slightly lower catalytic activity than the magnesium complex **2**. All polymer products were characterized by relatively low values of the dispersity $Đ_M$.‡ The principal difference of **3** when compared with **1** and **2** is that in the presence of **3** LA formed an atactic polymer, while **1** and **2** catalyzed heterotactic polylactic acid formation. The stereoselectivity of *rac*-lactide ROP catalyzed by Mg phenolates was observed[9] and modeled[25] in our recent works. Formation of atactic polylactic acid in the ROP catalyzed by **3** can result from complete destruction of the calcium phenolate within polymerization process.

In conclusion, magnesium phenolates are the most prospective ROP catalysts among phenolates of bivalent metals for both lactides and lactones. We have shown that the Mg complex **2**, after an activation with alcohol, serves as a classic single-site catalyst of 'living' polymerization, just like its BHT-containing analogue.[9]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.006.

References

1 Y. Sarazin and J.-F. Carpentier, *Chem. Rev.*, 2015, **115**, 3564.
2 C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832.
3 H.-Y. Chen, L. Mialon, K. A. Abboud and S. A. Miller, *Organometallics*, 2012, **31**, 5252.
4 Y. Gao, Z. Dai, J. Zhang, X. Ma, N. Tang and J. Wu, *Inorg. Chem.*, 2014, **53**, 716.
5 J. A. Wilson, S. A. Hopkins, P. M. Wright and A. P. Dove, *Macromolecules*, 2015, **48**, 950.
6 J. Ejfler, K. Krauzy-Dziedzic, S. Szafert, L. B. Jerzykiewicz and P. Sobota, *Eur. J. Inorg. Chem.*, 2010, 3602.
7 Y. Wang, W. Zhao, D. Liu, S. Li, X. Liu, D. Cui and X. Chen, *Organometallics*, 2012, **31**, 4182.
8 J. A. Wilson, S. A. Hopkins, P. M. Wright and A. P. Dove, *Polym. Chem.*, 2014, **5**, 2691.
9 I. E. Nifant'ev, A. V. Shlyakhtin, A. N. Tavtorkin, P. V. Ivchenko, R. S. Borisov and A. V. Churakov, *Catal. Commun.*, 2016, **87**, 106.
10 H.-J. Fang, P.-S. Lai, J.-Y. Chen, S. C. N. Hsu, W.-D. Peng, S.-W. Ou, Y.-C. Lai, Y.-J. Chen, H. Chung, Y. Chen, T.-C. Huang, B.-S. Wu and H.-Y. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2697.
11 C.-Y. Li, P.-S. Chen, S.-J. Hsu, C.-H. Lin, H.-Y. Huang and B.-T. Ko, *J. Organomet. Chem.*, 2012, **716**, 175.
12 K. Searles, B. L. Tran, M. Pink, C.-H. Chen and D. J. Mindiola, *Inorg. Chem.*, 2013, **52**, 11126.
13 K. Searles, K. Keijzer, C.-H. Chen, M.-H. Baik and D. J. Mindiola, *Chem. Commun.*, 2014, **50**, 6267.
14 K. Searles, P. J. Carroll, C.-H. Chen, M. Pink and D. J. Mindiola, *Chem. Commun.*, 2015, **51**, 3526.
15 K. Searles, B. Pinter, C.-H. Chen and D. J. Mindiola, *Organometallics*, 2014, **33**, 4192.
16 K. Searles, P. J. Carroll and D. J. Mindiola, *Organometallics*, 2015, **34**, 4641.
17 K. F. Tesh, D. J. Burkey and T. P. Hanusa, *J. Am. Chem. Soc.*, 1994, **116**, 2409.
18 J. Gromada, A. Mortreux, T. Chenal, J. W. Ziller, F. Leising and J.-F. Carpentier, *Chem. Eur. J.*, 2002, **8**, 3773.
19 U. Flörke, G. Henkel, A. Kuhn, N. Kuhn, S. Laufer and C. Maichle-Mößmer, *Z. Anorg. Allg. Chem.*, 2012, **638**, 730.
20 T. J. Boyle, S. D. Bunge, N. L. Andrews, L. E. Matzen, K. Sieg, M. A. Rodriguez and T. J. Headley, *Chem. Mater.*, 2004, **16**, 3279.
21 S. Enthaler, B. Eckhardt, S. Inoue, E. Irran and M. Driess, *Chem. Asian J.*, 2010, **5**, 2027.
22 M. M. Olmstead, P. P. Power and S. C. Shoner, *J. Am. Chem. Soc.*, 1991, **113**, 3379.
23 M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889.
24 M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583.
25 P. V. Ivchenko, A. V. Shlyakhtin and I. E. Nifant'ev, *Mendeleev Commun.*, 2017, **27**, 278.

‡ $Đ_M$ is often denoted as M_w/M_n (M_w is weight average molecular weight, M_n is number average molecular weight).

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